Nuclear Magnetic Relaxation in the Ferrimagnetic Chain Compound $NiCu(C_7H_6N_2O_6)(H_2O)_3{\cdot}2H_2O$: Three-Magnon Scattering?

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Recent proton spin-lattice relaxation-time (T_1) measurements on the ferrimagnetic chain compound $NiCu(C_7H_6N_2O_6)(H_2O)_3{\cdot}2H_2O$ are explained by an elaborately modified spin-wave theory. We give a strong evidence of *the major contribution to* $1/T_1$ *being made by the three-magnon scattering rather than the Raman one.*

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Low-frequency spin dynamics in magnetic systems is a long-standing problem and has recently attracted renewed interest due to the significant progress in designing low-dimensional materials such as chains and ladders. Nuclear magnetic resonance (NMR) is a powerful probe to their dynamic properties. The nuclear spin-lattice relaxation time T_1 is in particular eloquent of the collective motions of electronic spins and therefore we take a great interest in microscopically interpreting it. The spin-wave formalism has played a crucial role in this context. Van Kranendonk, Bloom [1], and Moriya [2] made their pioneering attempts to describe $1/T_1$ in terms of spin waves. Oguchi and Keffer [3] further developed the spin-wave analysis considering the three-magnon nuclear relaxation mechanism as well as the Raman one, whereas Pincus and Beeman [4] claimed that the three-magnon process was considerably underestimated in their argument, revealing further relaxation mechanism.

The spin-wave excitation energy is usually much larger than the nuclear resonance frequency and thus the single-magnon relaxation process is rarely of significance. The Raman process consequently plays a leading role in the nuclear spin-lattice relaxation. Because of the $(4S)^{-1}$-damping factor to the Holstein-Primakoff magnon series expansion, the multi-magnon scattering is much less contributive within the first-order mechanism, where a nuclear spin directly interacts with spin waves through the hyperfine coupling. However, the second-order mechanism, where a nuclear spin flip induces virtual spin waves which are then scattered thermally via the four-magnon exchange interaction, may generally enhance the relaxation rate. The Pincus-Beeman spin-wave nuclear relaxation theory is thus fascinating but works only far below the three-dimensional transition temperature. The conventional spin-wave theory applied to low-dimensional magnets ends in failure with diverging magnetizations. In such circumstances, Takahashi [5] gave a fine description of the low-dimensional ferromagnetic thermodynamics at low temperatures in terms of modified spin waves. His idea of introducing a constraint on the magnetization was developed for antiferromagnets [6,7] and ferrimagnets [8,9]. Random-bond ferromagnets [10] and frustrated antiferromagnets [11–13] were also discussed within this renewed spin-wave scheme.

The ferrimagnetic modified spin-wave theory is particularly powerful to investigate both static [14,15] and dynamic [16,17] properties. One-dimensional ferrimagnets have lately attracted much attention especially in the context of designing molecule-based ferromagnets [18]. A series of bimetallic chain compounds [19] are typical examples and some of them were indeed assembled into a ferromagnetic lattice. Another approach [20] consists of bringing into interaction metal ions and stable organic radicals. Homometallic systems can exhibit distinct ferrimagnetism of topological origin [21,22]. Such synthetic endeavors have stimulated several experimentalists [23,24] to measure T_1 on ferrimagnetic chain compounds. Thus motivated, here we make a systematic spin-wave analysis on the nuclear spin dynamics in one-dimensional Heisenberg ferrimagnets, which has been pending for the past decades without any suitable spin-wave scheme. Our goal is to show a strong evidence of *the proton spin relaxation in the title compound being mediated by the three-magnon scattering rather than the Raman one.*

First of all our scheme [8] of modifying the spin-wave theory is distinct from the original idea proposed by Takahashi [6] and Hirsch *et al.* [7]. Their way of suppressing the divergent sublattice magnetizations consists of diagonalizing an effective Hamiltonian with a Lagrange multiplier included subject to zero staggered magnetization. The thus-obtained energy spectrum necessarily depends on temperature and fails to reproduce the Schottky peak of the specific heat [25]. In order to obtain better thermodynamics, we first diagonalize the Hamiltonian keeping the dispersion relations free from temperature and then introduce a Lagrange multiplier in order to minimize the free energy subject to zero staggered magnetization. This scheme is highly successful in describing the magnetic susceptibility as well as the specific heat [25] and therefore guarantees our exploration of the one-dimensional ferrimagnetic dynamics over a wide temperature range.

We consider ferrimagnetic Heisenberg chains of alternating spins S and s, as described by the Hamiltonian

$$\mathcal{H}=\sum_{n=1}^{N}\left[J\boldsymbol{S}_n\cdot(\boldsymbol{s}_{n-1}+\boldsymbol{s}_n)-(g_S S_n^z+g_s s_n^z)\mu_{\rm B}H\right]. \quad (1)$$

Introducing bosonic operators for the spin deviation in each sublattice via $S_i^+ = (2S - a_{-:i}^\dagger a_{-:i})^{1/2} a_{-:i}$, $S_i^z = S - a_{-:i}^\dagger a_{-:i}$, $s_i^+ = a_{+:i}^\dagger (2s - a_{+:i}^\dagger a_{+:i})^{1/2}$, $s_i^z = -s + a_{+:i}^\dagger a_{+:i}$, and assuming that $O(S) = O(s)$, we expand the Hamiltonian with respect to $1/S$ as $\mathcal{H} = \mathcal{H}_2 + \mathcal{H}_1 + \mathcal{H}_0 + O(S^{-1})$, where $\mathcal{H}_i$ contains the $O(S^i)$ terms. $\mathcal{H}_2 \equiv -2SsJN$ is the classical ground-state energy, while $\mathcal{H}_1$ describes linear spin-wave excitations and is diagonalized in the momentum space as

$$\begin{aligned}\mathcal{H}_1 = &-(S+s)JN - \left[g_S(S+\tfrac{1}{2}) - g_s(s+\tfrac{1}{2})\right]\mu_{\rm B}HN \\ &+(g_S - g_s)\mu_{\rm B}H\textstyle\sum_k \dfrac{S + s + (g_S - g_s)\mu_{\rm B}H/2J}{2\omega_k} \\ &+J\textstyle\sum_k \omega_k + J\sum_k \sum_{\sigma=\pm} \omega_k^\sigma \alpha_{\sigma:k}^\dagger \alpha_{\sigma:k}, \end{aligned} \tag{2}$$

where $\alpha_{\sigma:k}^\dagger \equiv a_{\sigma:k}^\dagger \cosh\theta_k + a_{-\sigma:k} \sinh\theta_k$, provided $\tanh 2\theta_k = 2\sqrt{Ss}\cos(k/2)/[S + s + (g_S - g_s)\mu_{\rm B}H/2J]$, creates a spin wave of ferromagnetic ($\sigma = -$) or antiferromagnetic ($\sigma = +$) aspect [26], whose energy is given by $\omega_k^\sigma = \omega_k + \sigma[S - s - (g_S + g_s)\mu_{\rm B}H/2J]$ with $\omega_k \equiv \{[S + s + (g_S - g_s)\mu_{\rm B}H/2J]^2 - 4Ss\cos^2(k/2)\}^{1/2}$. Minimizing the free energy under the condition of zero staggered magnetization [16], we obtain the optimum distribution functions $\bar{n}_k^\sigma \equiv \langle \alpha_{\sigma:k}^\dagger \alpha_{\sigma:k} \rangle$.

The hyperfine interaction is generally expressed as

$$\begin{aligned}\mathcal{H}_{\rm hf} = &\, g_S\mu_{\rm B}\hbar\gamma_{\rm N} I^+ \textstyle\sum_n \left(\frac{1}{2}A_n^- S_n^- + A_n^z S_n^z\right) \\ &+ g_s\mu_{\rm B}\hbar\gamma_{\rm N} I^+ \textstyle\sum_n \left(\frac{1}{2}B_n^- s_n^- + B_n^z s_n^z\right), \end{aligned} \tag{3}$$

where A_n^σ (B_n^σ) is the dipolar coupling tensor between the nuclear and nth larger (smaller) electronic spins. Since $\mathcal{H}_0$ and $\mathcal{H}_{\rm hf}$ are both much smaller than $\mathcal{H}_1$, they act as perturbative interactions to the linear spin-wave system. If we consider up to the second-order perturbation with respect to $\mathcal{V} \equiv \mathcal{H}_0 + \mathcal{H}_{\rm hf}$, the probability of a nuclear spin being scattered from the state of $I^z = m$ to that of $I^z = m + 1$ is given by

$$W = \frac{2\pi}{\hbar} \sum_f \left| \left\langle f \middle| \mathcal{V} + \sum_{m(\neq i)} \frac{\mathcal{V}|m\rangle\langle m|\mathcal{V}}{E_i - E_m} \middle| i \right\rangle \right|^2 \delta(E_i - E_f), \tag{4}$$

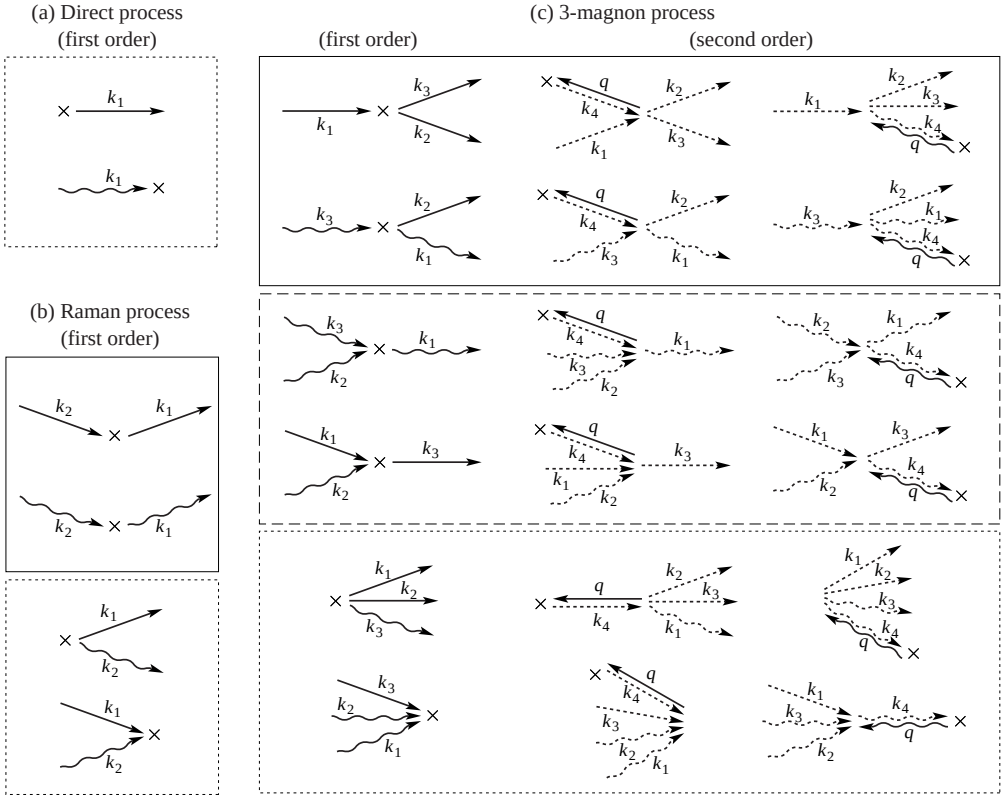

FIG. 1. Diagrammatic representation of various nuclear spin-lattice relaxation processes. Solid arrows, designating spin waves which are emitted in the first-order processes, induce a nuclear spin flip (×) via the hyperfine interaction, while broken arrows, depicting four-magnon exchange correlations, thermally scatter the first-order spin waves as *virtual excitations*, where spin waves of ferromagnetic and antiferromagnetic aspect are distinguishably drawn by straight and wavy arrows, respectively. (a) The first-order direct (single-magnon) relaxation processes; (b) The first-order Raman (two-magnon) relaxation processes; (c) The first-order and second-order three-magnon relaxation processes, where $q = -k_4 \equiv k_1 - k_2 - k_3$, are related to each other through nonlinear equations and are therefore inseparable. Considering the nuclear-electronic energy conservation, processes in solid and dotted frames are of great and little significance, respectively, whereas those in broken frames are relevant according to the constituent spins S and s.

where i and f designate the initial and final states of the unperturbed electronic-nuclear spin system. Then we find that $T_1 = (I-m)(I+m+1)/2W$. Equation (4) contains various relaxation processes but their explicit formulae will be presented elsewhere. We instead diagrammatically show them in Fig. 1. Due to the considerable difference between the nuclear and electronic energy scales, $\hbar\omega_{\rm N} \ll J$, the direct process, involving a single spin wave, is rarely of significance. Considering further that the antiferromagnetic spin waves are higher in energy than the ferromagnetic ones, $\omega_k^- < \omega_k^+$, at moderate fields, the intraband spin-wave scattering dominates the Raman relaxation rate $1/T_1^{(2)}$, whereas both the intraband and interband spin-wave scatterings contribute to the three-magnon relaxation rate $1/T_1^{(3)}$. Within the first-order mechanism, $1/T_1^{(3)}$ is much smaller than $1/T_1^{(2)}$ [3]. However, the first-order relaxation rate is generally enhanced through the second-order mechanism. We consider the leading second-order process, that is, the exchange-scattering-induced three-magnon relaxation, as well as the first-order process. The second-order single-magnon and Raman processes, containing three and two virtual magnons, respectively, are much more accidental due to the momentum conservation and much less contributive due to the $(4S)^{-1}$-damping factor in the Holstein-Primakoff magnon series expansion.

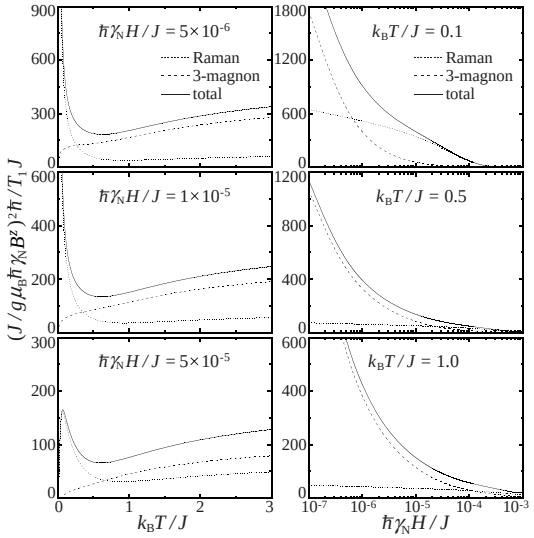

FIG. 2. Modified spin-wave calculations of typical temperature (the left three) and field (the right three) dependences of the nuclear spin-lattice relaxation rate, where $g_S = g_s \equiv g$, $A^\tau/B^\tau = 1$, and $(B^-/B^z)^2 = 4$. $1/T_1^{(2)}$ and $1/T_1^{(3)}$ are plotted by dotted and broken lines, respectively, while $1/T_1^{(2)} + 1/T_1^{(3)} \equiv 1/T_1$, which is observable, by solid lines.

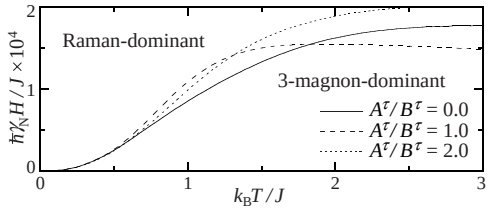

FIG. 3. The crossover point as a function of temperature and an applied field, where $g_S = g_s$ and $(B^-/B^z)^2 = 4$.

We calculate the case of $(S,s) = (1,\frac{1}{2})$, which is relevant to several major materials [20,22,27], assuming that the Fourier components of the coupling constants have little momentum dependence [24] as $\sum_n e^{ikn}A_n^\tau \equiv A_k^\tau \simeq A^\tau$ and $\sum_n e^{ikn}B_n^\tau \equiv B_k^\tau \simeq B^\tau$ $(\tau = -, z)$. Figure 2 shows $1/T_1$ as a function of temperature and an applied field. The exchange-scattering-enhanced three-magnon relaxation rate generally grows into a major contribution to $1/T_1$ with increasing temperature and decreasing field. As temperature increases, $\bar{n}_k^-$ decreases at $k \simeq 0$ but otherwise increases [28]. In one dimension, excitations at $k \simeq 0$ predominate in the Raman process, while all the excitations are effective in the three-magnon process. $1/T_1^{(2)}$ and $1/T_1^{(3)}$ are hence decreasing and increasing functions of temperature, respectively, unless temperature is so high as to activate the antiferromagnetic spin waves. The field dependences of $1/T_1^{(2)}$ and $1/T_1^{(3)}$ are also in striking contrast. At moderately low temperatures and weak fields, $\hbar\omega_{\rm N} \ll k_{\rm B}T \ll J$, we find that $1/T_1^{(2)} \propto e^{-(g_S+g_s)\mu_{\rm B}H/2k_{\rm B}T}K_0(\hbar\omega_{\rm N}/2k_{\rm B}T)$, where K_0 is the modified Bessel function of the second kind and behaves as $K_0(\hbar\omega_{\rm N}/2k_{\rm B}T) \simeq 0.80908 - \ln(\hbar\omega_{\rm N}/k_{\rm B}T)$. Thus the field dependence of $1/T_1^{(2)}$ is initially logarithmic and then turns exponential with increasing field. Equation (4) claims that $1/T_1^{(3)}$ is much less analyzable but should exhibit much stronger power-law diverging behavior with decreasing field. Therefore, the three-magnon relaxation process predominates over the Raman one at weak fields.

In Fig. 3 we plot *the crossover points* on which $1/T_1^{(2)} = 1/T_1^{(3)}$. A Raman-to-three-magnon crossover may generally be detected with increasing temperature and decreasing field. The ferrimagnetic nuclear spin-latticerelaxation is sensitive to another adjustable parameter A^τ/B^τ, that is, the location of the probe nuclei. At the special location of $A^\tau/B^\tau \sim (d_s/d_S)^3 \simeq (S/s)^\sigma$, where d_S (d_s) is the distance between the nuclear and larger (smaller) electronic spins, the σ excitation mode hardly mediates the nuclear spin relaxation [28]. For $(S,s) = (1,\frac{1}{2})$, the lower-lying ferromagnetic spin waves are almost invisible to the nuclear spin located as A^τ/B^τ

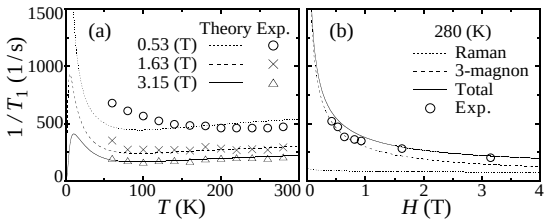

FIG. 4. Proton spin relaxation-time measurements on $NiCu(C_7H_6N_2O_6)(H_2O)_3{\cdot}2H_2O$ [24] compared with our theory. (a) $1/T_1$ as a function of temperature at various values of an applied field; (b) $1/T_1$ as a function of an applied field at 280 K, where $1/T_1^{(2)}$ and $1/T_1^{(3)}$ are also plotted by dotted and broken lines, respectively.

$\simeq 1/2$ and therefore its relaxation rate stays extremely small. Any T_1 measurements should be performed away from such magic points.

We are further excited to compare our theory with recent experimental findings. Fujiwara and Hagiwara [24] measured T_1 for proton nuclei in the bimetallic chain compound $NiCu(C_7H_6N_2O_6)(H_2O)_3{\cdot}2H_2O$ [27] comprising ferrimagnetic chains with alternating octahedral Ni^{2+} and square-pyramidal Cu^{2+} ions. The measured susceptibility [29] suggests that $J/k_B \simeq 121\,K$, $g_S = 2.22$, and $g_s = 2.09$. Comparative measurements on the D_2O-substituted samples [24] indicate that protons relevant to the T_1 findings are located in close vicinity to Cu spins. Then, considering that the dipolar coupling strength is in proportion to the inverse cubic distance, we may set the coupling constants for $A^\tau/B^\tau = 0$. Conditioning further that $B^z = 1.37 \times 10^{20}\,T^2/J$ and $(B^-/B^z)^2 = 5$, which can be consistent with the crystalline structure [27], we plot calculations together with the observations in Fig. 4. The ferromagnetic and antiferromagnetic spin waves contribute different temperature dependences to $1/T_1$ and give the decreasing and then increasing behavior in Fig. 4(a). Considering that there may be larger uncertainty in the experimental findings for $1/T_1$ at lower temperatures and weaker fields [24], the theoretical and experimental findings are in good agreement and the slight discrepancy between them may be attributable, for instance, to weak momentum dependence of B_k^τ and the protons of wide distribution. Figure 4(b) more impressively demonstrates the relevance of the three-magnon scattering to the proton spin relaxation. *The strong field dependence can never be explained by the Raman process.* Since $1/T_1^{(3)}$ within the first-order mechanism stays much smaller than the observations, *the exchange-scattering-induced three-magnon process is essential in interpreting such accelerated relaxation.* We are eager to have reliable observations at lower temperatures and weaker fields. We call for more extensive NMR measurements using as probes ^1H, ^{63}Cu, and ^{55}Mn nuclei on the family material $MnCu(C_7H_6N_2O_6)(H_2O)_3{\cdot}2H_2O$ [27] as well as that of present interest.

There exist pioneering T_1 measurements on the layered ferromagnet $CrCl_3$ [30] and the coupled-chain antiferromagnet $CsMnCl_3{\cdot}2H_2O$ [31], which give evidence of the relevant three-magnon scattering. However, they are both, in some sense, *classical* findings under the existing three-dimensional long-range order. Without any reliable spin-wave formulation in one dimension, no author has explored *quantum* ferrimagnetic dynamics with particular interest in multi-magnon scattering beyond the Raman mechanism. The present calculation is *the first evidence of the three-magnon scattering dominating the one-dimensional nuclear spin relaxation* and motivate extensive T_1 measurements on various one-dimensional quantum ferrimagnets.

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